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(54) **Liquid silicone rubber coating composition**

(57) A curable liquid silicone rubber coating composition is disclosed. This composition exhibits excellent infiltrability and is used to form thin coatings on synthetic fabrics, without using a dilution solvent. The cured composition is a tackfree coating film with excellent adherence to synthetic fabrics. The curable composition in-

cludes: (A) a diorganopolysiloxane that contains at least 2 alkenyl groups in each molecule; (B) an organopolysiloxane resin; (C) an inorganic filler; (D) an organohydrogenopolysiloxane that contains at least 2 silicon-bonded hydrogen atoms in each molecule; (E) a platinum group catalyst; (F) an epoxy-functional organosilicon compound; and (G) an organotitanium compound.

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**Description**

The present invention relates to liquid silicone rubber coating compositions that are used, for example, with automotive air bags. More particularly, the present invention is a liquid silicone rubber coating composition that cures into a silicone rubber coating film with a tackfree surface which has an excellent capacity to form thin coating films without the use of solvent. The cured coating exhibits extensibility, and in particular exhibits an adhesive strength capable of withstanding the shock of high-temperature expansion or inflation.

Base fabrics comprising a synthetic fiber fabric (e.g., of nylon 66) coated with silicone rubber offer the advantages of good thermal characteristics, nonflammability, and excellent resistance to deterioration with the passage of time. These advantages have led to their use in automotive air bags.

A diluting solvent such as toluene or xylene is generally used when coating the silicone rubber on synthetic fabric to obtain a uniform and thin coating and to achieve strong bonding with the base fabric. However, a liquid silicone rubber composition that is coatable without the use of solvent has been introduced in response to recent environmental restrictions to eliminate or reduce the use of solvents (JP-A 5-214295). A drawback to fabrics coated with this composition is that the surface of the applied film presents some residual tack even after cure into silicone rubber. When left as is, this residual tack impairs the processability during such operations as sewing and also causes adjacent films of the coating to stick to each other during storage of the folded fabric. These problems have made it necessary to dust the surface of the applied films with talc, calcium carbonate, or clay.

The curable liquid silicone rubber composition of the present invention overcomes the drawbacks of the prior art. Our inventive composition contains both a special class of organosilicon compound and an organotitanium compound. The uncured composition exhibits good infiltrability into synthetic fabrics and excellent capacity to be coated out into thin films on synthetic fabrics, without the inclusion of an organic solvent. unexpectedly, the cured composition has strong adherence to synthetic fabrics and exhibits a low surface tack.

It is an object of the present invention to provide a curable liquid silicone rubber coating composition that can be coated on synthetic fabrics and which exhibits excellent infiltrability of synthetic fabrics and excellent capacity to form thin coatings thereon, without using a dilution solvent.

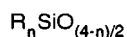
It is another object to provide a curable liquid silicone rubber coating composition that cures to form a tackfree coating film that has excellent adherence to synthetic fabrics.

The curable liquid silicone coating composition of the present invention comprises:

- (A) 100 weight parts of a diorganopolysiloxane that has a viscosity at 25°C of 100 to 100,000 mPa.s (centipoise) and that contains at least 2 alkenyl groups in each molecule;
- (B) from 5 to 100 weight parts of organopolysiloxane resin;
- (C) from 5 to 100 weight parts inorganic filler;
- (D) organohydrogenopolysiloxane that contains at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity that affords a value from 0.6 : 1 to 20 : 1 for the ratio of the number of moles of silicon-bonded hydrogen in this component to the number of moles of alkenyl in component (A);
- (E) platinum group catalyst, in a quantity that affords 0.1 to 500 weight parts of platinum group metal for each one million weight parts of component (A);
- (F) from 0.1 to 20 weight parts of epoxy-functional organosilicon compound; and
- (G) from 0.1 to 5 weight parts of an organotitanium compound.

The diorganopolysiloxane (A) of the present invention is the base ingredient of our composition. This component must contain at least 2 alkenyl groups in each molecule to obtain a rubbery elastic silicone rubber coating film from the cure of the claimed composition.

The subject organopolysiloxane is a substantially linear organopolysiloxane as defined by the following formula



wherein R represents substituted or unsubstituted monovalent hydrocarbon groups as exemplified by alkyl groups such as methyl, ethyl, and propyl; alkenyl groups such as vinyl or allyl; aryl groups such as phenyl; and haloalkyl groups such as 3,3,3-trifluoropropyl. n in the preceding formula is from 1.9 to 2.1. This diorganopolysiloxane has a viscosity at 25°C from 100 to 100,000 mPa.s (centipoise). Viscosities at 25°C from 1,000 to 50,000 mPa.s (centipoise) are more preferred based on considerations of ease of mixing and the strength of the ultimately obtained silicone rubber coating. The component (A) under consideration is exemplified by dimethylvinylsiloxy-endblocked dimethylpolysiloxanes, dimethylvinylsiloxy-endblocked dimethylsiloxane-methylvinylsiloxane copolymers, dimethylvinylsiloxy-endblocked dimethylsiloxane-methylphenylsiloxane copolymers, and dimethylvinylsiloxy-endblocked methyl(3,3,3-trifluoropropyl)

siloxane-methylvinylsiloxane copolymers.

The organopolysiloxane resin (B) is a component that improves the mechanical strength of the silicone rubber coating film, and in particular improves the infiltrability and adherence of our silicone rubber coating composition for the synthetic fabrics used in air bags. This organopolysiloxane resin is exemplified by the following: resins composed of the  $(\text{CH}_3)_3\text{SiO}_{1/2}$  and  $\text{SiO}_{4/2}$  units; resins composed of the  $(\text{CH}_3)_3\text{SiO}_{1/2}$ ,  $(\text{CH}_2=\text{CH})\text{SiO}_{3/2}$ , and  $\text{SiO}_{4/2}$  units; resins composed of the  $(\text{CH}_2=\text{CH})(\text{CH}_3)_2\text{SiO}_{1/2}$  and  $\text{SiO}_{4/2}$  units; and resins composed of the  $(\text{CH}_2=\text{CH})(\text{CH}_3)_2\text{SiO}_{1/2}$ ,  $(\text{CH}_2=\text{CH})\text{SiO}_{3/2}$ , and  $\text{SiO}_{4/2}$  units.

Among these, vinyl-functional resins are preferred because they improve the strength of our silicone rubber coating film. Preferred resins are liquid at room temperature, or are solid so long as still compatible with component (A). Based on the objectives of improving the infiltrability into synthetic fabrics while simultaneously improving the capacity for coating out into a thin film, component (B) is added at from 5 to 80 weight parts and preferably at from 10 to 80 weight parts.

The inorganic filler (C) can be those fillers whose use in silicone rubbers is known from the art for such purposes as reinforcement, viscosity adjustment, improving heat stability, and improving nonflammability. This inorganic filler is exemplified by reinforcing fillers such as silica (e.g., fumed silica, precipitated silica and calcined silica), fumed titanium oxide; nonreinforcing fillers such as crushed quartz, diatomaceous earth, iron oxide, aluminum oxide, calcium carbonate and magnesium carbonate; and the aforesaid fillers treated with an organosilicon compound such as organosilane or organopolysiloxane. Silicas with specific surface areas of at least  $50 \text{ m}^2/\text{g}$  are preferred. The optimal filler is a surface-treated silica whose surface has been preliminarily treated with compounds such as organosilane, organosilazane and diorganocyclopolsiloxane.

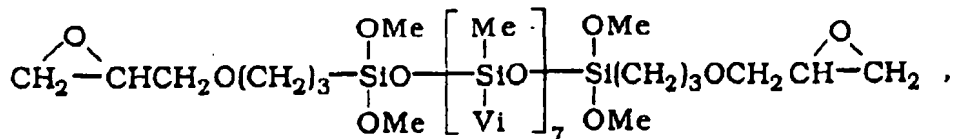
The amount of component (C) used in the composition of this invention will vary with the particular type of inorganic filler, but is generally in the range from 5 to 100 weight parts per 100 weight parts of component (A). In the particular instance where silica is the inorganic filler, the silica should be added at from 5 to 15 weight parts per 100 weight parts of component (A). The use of more than 15 weight parts of silica causes the composition to have an excessively high viscosity and thereby impairs solventless coating on the base fabric. Contrastingly, the use of less than 5 weight parts results in a decline in the mechanical strength of the silicone rubber coating film.

Component (D), which is the crosslinker for our composition, is organopolysiloxane that contains at least 2 silicon-bonded hydrogen atoms in each molecule. This organopolysiloxane is exemplified by the following: trimethylsiloxy-endblocked methylhydrogenpolysiloxanes, trimethylsiloxy-endblocked dimethylsiloxane-methylhydrogensiloxane copolymers, dimethylphenylsiloxy-endblocked methylphenylsiloxane-methylhydrogensiloxane copolymers, cyclic methylhydrogenpolysiloxanes, and copolymers composed of the dimethylhydrogensiloxy and  $\text{SiO}_{4/2}$  units.

The viscosity of the organopolysiloxane of component (D) is generally in the range from 1 to 1,000 mPa.s (centipoise). The subject organohydrogenpolysiloxane is added in a quantity that affords from 0.6 : 1 to 20 : 1, and preferably from 1 : 1 to 10 : 1, for the ratio of the number of moles of silicon-bonded hydrogen in the organohydrogenpolysiloxane to the number of moles of alkenyl groups in component (A).

The platinum group catalyst used as component (E) in this invention is a curing catalyst for our composition. This component is exemplified by very finely divided platinum, platinum black, chloroplatinic acid, platinum tetrachloride, chloroplatinic acid-olefin complexes, alcohol solutions of chloroplatinic acid, chloroplatinic acid-alkenylsiloxane complexes, rhodium compounds, and palladium compounds. The platinum group catalyst is generally used at 0.1 to 500 weight parts, and preferably at 1 to 50 parts, per 1,000,000 weight parts of component (A). A satisfactory development of the reaction will not occur at less than 0.1 weight part, while exceeding 500 weight parts is uneconomical.

The epoxy-functional organosilicon compound (F) improves the adherence of the composition of the present invention for the synthetic fabrics used in air bags. The subject organosilicon compound is exemplified by epoxy-functional organoalkoxysilanes such as gamma-glycidyloxypropyltrimethoxysilane or beta(3,4-epoxycyclohexyl)ethyltrimethoxysilane; and by epoxy-functional organopolysiloxanes that also contain silicon-bonded vinyl and alkoxy, epoxy-functional organopolysiloxanes that also contain silicon-bonded hydrogen, and epoxy-functional organopolysiloxanes that also contain silicon-bonded hydrogen and alkoxy. The following compounds are specific examples of the said epoxy-functional organopolysiloxanes (where Me = methyl and Vi = vinyl).



In addition to the components (A) to (G), the composition of the present invention preferably also contains a cure retarder as a component (H). This optional component is exemplified by alkyne alcohols such as 3-methyl-1-butyn-3-ol, 3,5-dimethyl-1-hexyn-3-ol, and phenylbutynol; ene-yne compounds such as 3-methyl-3-penten-1-yne, or 3,5-dimethyl-3-hexen-1-yne; tetramethyltetrahexenylcyclotetrasiloxane and benzotriazole. The cure retarder is generally used at 0.01 to 10 weight parts per 100 weight parts of component (A). The composition of this invention is prepared simply by the preparation of a homogeneous mixture using a mixer, such as a kneader mixer, kneader mixer equipped with a ram cover, Ross™ mixer, and so forth. Various other optional components, for example, pigments, heat stabilizers, and the like can be added insofar as the object of the invention is not impaired.

To produce a silicone rubber-coated fabric, the composition of our invention is coated onto the synthetic fabric followed by introduction into a hot-air drying oven for heating and curing. The silicone rubber composition is generally applied at a rate not exceeding 80 g/m<sup>2</sup>. The heating and curing affords a flexible coated fabric in which the silicone rubber coating film and synthetic fabric have been tightly bonded into a single body at an adhesive strength of at least 1.5 kgf/cm. Moreover, no tack is exhibited by the surface of the coating film on the coated fabric. As a result, even in the absence of dusting with, for example, talc or calcium carbonate, this tackfree condition for our claimed coated fabrics makes possible an excellent processability in operations such as sewing, and also eliminates sticking between adjacent coating films during storage in a folded state.

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denotes "weight parts," the values reported for the viscosity were measured at 25°C, Me represents the methyl group, and Vi represents the vinyl group.

#### Example 1

100 parts dimethylvinylsiloxyl-terminated dimethylpolysiloxane with a viscosity of 2,000 mPa.s (centipoise) and 30 parts vinyl-functional methylpolysiloxane resin (vinyl content = 5.6%, viscosity = 230 mPa.s [centipoise]) composed of the  $\text{Vi}(\text{Me})_2\text{SiO}_{1/2}$  and  $\text{SiO}_{4/2}$  units were introduced into a Ross™ mixer. The following were subsequently added with mixing to homogeneity: 12 parts fumed silica with a specific surface area of 200 m<sup>2</sup>/g, 5 parts hexamethyldisilazane as surface-treatment agent for the silica, and 2 parts water. Heating in a vacuum then afforded a liquid silicone rubber base with a fluid consistency.

The following were mixed to homogeneity into 100 parts of this liquid silicone rubber base to yield a liquid silicone rubber coating composition: 6 parts methylhydrogenpolysiloxane with the average molecular formula  $\text{Me}_3\text{SiO}$  ( $\text{MeH-SiO}$ )<sub>6</sub>( $\text{Me}_2\text{SiO}$ )<sub>4</sub> $\text{SiMe}_3$ , 0.5 part chloroplatinic acid-divinyltetramethyldisiloxane complex (platinum concentration = 0.4 weight%), 0.4 part 3,5-dimethyl-1-hexyn-3-ol as curing inhibitor, 1 part gammaglycidoxypolytrimethoxysilane as adhesion promoter, and 0.5 part tetrabutyl titanate as tack inhibitor. This composition had a viscosity of 26,000 mPa.s (centipoise). The composition was coated on a nylon 66 fiber fabric 4.67 x 10<sup>-5</sup> kg/m (420 denier) and was cured by heating for 2 minutes at 180°C. The fabric coating technique consisted of application of our liquid silicone rubber coating composition with a coater using the minimum quantity capable of giving a uniform and even coating. Two coated and cured surfaces of this coated fabric were laid one on top of the other and bonded to one another through an interposed layer of a room-temperature-curable silicone rubber adhesive (SE9145 RTV from Dow Corning Toray Silicone Company, Limited). After curing at room temperature for 7 days, a strip 2.5 cm in width by 10 cm in length was cut out and subjected to a peel test, during which the adhesive strength was measured. A Scott™ flexing test (ASTM D430-95) was also run using a Scott™ flexing machine: delamination of the thin silicone rubber coating film from the surface of the fabric was visually inspected after 1,000 cycles with a 2 kg flexing load. The tack of the surface of the coating film was evaluated by touch with a finger.

To measure the infiltrability, a synthetic fabric for air bag service was cut into a strip (2 cm width by 10 cm length) and this strip was hung vertically. Its bottom end was then dipped (0.5 mm) into the liquid silicone rubber composition. This setup was allowed to stand undisturbed for 24 hours at room temperature, at which point the infiltration distance of the liquid silicone rubber composition into the base fabric was measured. A small quantity of a pigment was added to the silicone rubber composition in this test to facilitate determination of the area of infiltration.

The results of these property measurements are reported in Table 1.

#### Comparative Example 1

A liquid silicone rubber coating composition was prepared as in Example 1, but without the addition of the tetrabutyl titanate of Example 1. The properties of this composition were measured as in Example 1, and the results are reported in Table 1.

Table 1

Test/Property	Example 1	Comparative Example 1
durometer of the silicone rubber (JIS A)	52	50
minimum coating weight (g/m <sup>2</sup> )	40	40
adhesive strength (kgf/cm)	3.5	2.5
Scott™ flexing test	passes	passes
infiltrability (cm)	2.3	2.4
tack	none	present

#### Example 2 and Comparative Example 2

For Example 2 and Comparative Example 2, the liquid silicone rubber coating compositions prepared in Example 1 and Comparative Example 1 were respectively coated as in Example 1 on a polyester fiber fabric 4.67 x 10<sup>-5</sup> kg/m (420 denier) to give silicone rubber-coated fabrics. The properties of these fabrics were measured, and these results are reported in Table 2.

Table 2

Test/Property	Example 2	Comparative Example 2
durometer of the silicone rubber (JIS A)	52	50
minimum coating weight (g/m <sup>2</sup> )	42	44
adhesive strength (kgf/cm)	3.0	2.2
Scott flexing test	passes	passes
infiltrability (cm)	2.0	2.2
tack	none	present

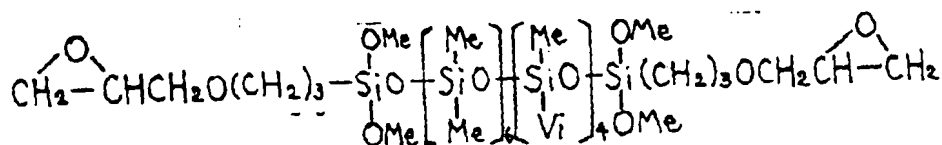
Example 3 and Comparative Example 3

100 parts dimethylvinylsiloxyl-endblocked dimethylpolysiloxane with a viscosity of 12,000 mPa.s (centipoise) and 20 parts vinyl-functional methylpolysiloxane resin (vinyl weight = 5.6%, viscosity = 230 mPa.s [centipoise]) composed of the  $\text{Vi}(\text{Me})_2\text{SiO}_{1/2}$  and  $\text{SiO}_{4/2}$  units were introduced into a Ross™ mixer. 10 parts fumed silica (specific surface area = 200 m<sup>2</sup>/g) that had been preliminarily treated with hexamethyldisilazane was then added with mixing to homogeneity to yield a liquid silicone rubber base with a fluid consistency.

The following were mixed to homogeneity into 100 parts of this liquid silicone rubber base to yield a liquid silicone rubber coating composition: 3 parts methylhydrogenpolysiloxane with the average molecular formula



(silicon-bonded hydrogen content = 1.57 weight%), 0.5 part chloroplatinic acid-divinyltetramethyldisiloxane complex (platinum concentration = 0.4 weight%), 0.1 part methyltris(3-methyl-1-butyn-3-oxy)silane as curing inhibitor, as adhesion promoter 1 part of the epoxy-functional organosiloxane compound



and 2 parts diisopropoxybis(ethyl acetoacetate)titanium as tack inhibitor. This liquid silicone rubber composition had a viscosity of 58,000 mPa.s (centipoise). This composition was coated as in Example 1 on nylon 66 fiber fabric and the adherence, capacity for coating out into a thin film, infiltrability, and tack were evaluated. In the Comparative Example 3, a liquid silicone rubber coating composition was prepared as above, but without the addition of diisopropoxybis(ethyl acetoacetate)titanium. The results of the evaluations are reported in Table 3.

Table 3

Test/Property	Example 3	Comparative Example 3
durometer of the silicone rubber (JIS A)	47	44
minimum coating weight (g/m <sup>2</sup> )	42	45
adhesive strength (kgf/cm)	3.3	2.2
Scott™ flexing test	passes	passes
infiltrability (cm)	1.8	1.8
tack	none	present

Because our liquid silicone rubber coating composition comprises components (A) to (G) and in particular because it contains the organotitanium compound (G), in addition to the organosiloxane resin (B) and epoxy-functional organosilicon compound (F), it is characterized by: an excellent infiltrability for and strong adherence to synthetic fabrics (e.g., of nylon 66); an excellent capacity to form thin coating films on synthetic fabrics; and a facile coatability without the use of a dilution solvent. Moreover, since the surface of the cured coated film on silicone rubber-coated fabric

afforded by the application of the instant silicone rubber coating composition is tackfree, even without dusting the coated film surface with, for instance, talc or calcium carbonate, this fabric has an excellent processability in such operations as sewing and is free of the problem of sticking between adjacent coating films during storage in a folded condition.

## Claims

1. A curable liquid silicone rubber coating composition comprising:

(A) 100 weight parts of a diorganopolysiloxane that has a viscosity at 25°C of 100 to 100,000 mPa.s (centipoise) and that contains at least 2 alkenyl groups in each molecule;  
 (B) 5 to 100 weight parts of an organopolysiloxane resin;  
 (C) 5 to 100 weight parts of an inorganic filler;  
 (D) an organohydrogenpolysiloxane that contains at least 2 silicon-bonded hydrogen atoms in each molecule

said organohydrogenpolysiloxane (D) being present in a quantity such that the ratio of the number of moles of silicon-bonded hydrogen in (D) to the number of moles of said alkenyl groups in (A) is from 0.6 : 1 to 20 : 1;

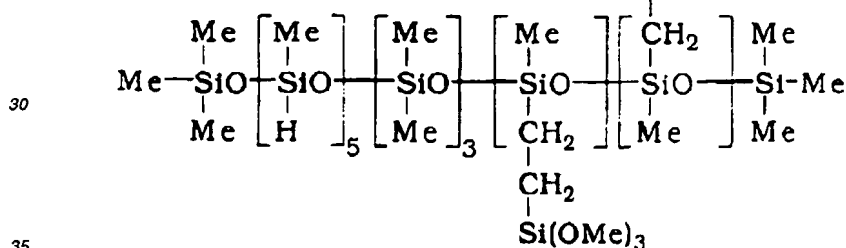
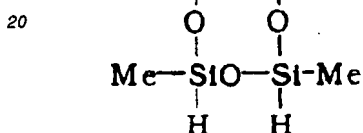
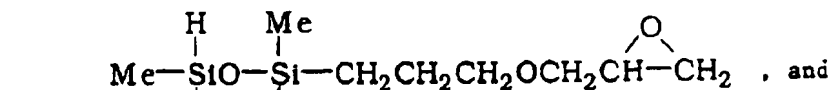
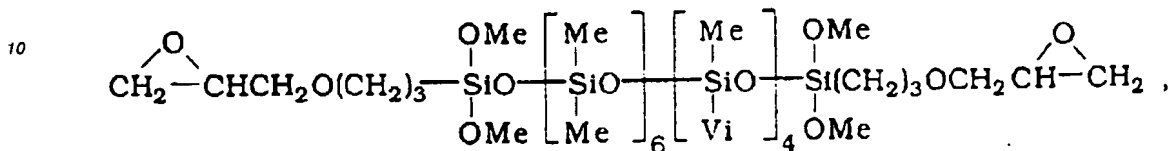
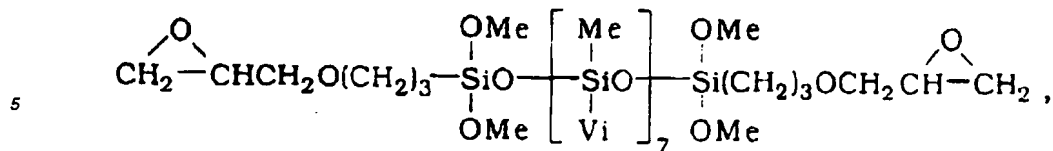
(E) 0.1 to 500 weight parts of a platinum group catalyst per one million weight parts of component (A);  
 (F) 0.1 to 20 weight parts of an epoxy-functional organosilicon compound; and  
 (G) 0.1 to 5 weight parts of an organotitanium compound.

2. A curable liquid silicone rubber coating composition in accordance with Claim 1 wherein component (G) is an organotitanate ester or a titanium chelate.

3. A composition in accordance with Claim 1 or Claim 2 wherein said diorganopolysiloxane (A) is selected from the group consisting of dimethylvinylsiloxy-endblocked dimethylpolysiloxanes, dimethylvinylsiloxy-endblocked dimethylsiloxy-methylvinylsiloxy copolymers, dimethylvinylsiloxy-endblocked dimethylsiloxy-methylphenylsiloxy copolymers, and dimethylvinylsiloxy-endblocked methyl(3,3,3-trifluoropropyl)siloxy-methylvinylsiloxy copolymers.

4. A composition in accordance with any of Claims 1 to 3 wherein said organopolysiloxane resin (B) is selected from the group consisting of resins composed of the  $(\text{CH}_3)_3\text{SiO}_{1/2}$  and  $\text{SiO}_{4/2}$  units, resins composed of the  $(\text{CH}_3)_3\text{SiO}_{1/2}$ ,  $(\text{CH}_2=\text{CH})\text{SiO}_{3/2}$ , and  $\text{SiO}_{4/2}$  units, resins composed of the  $(\text{CH}_2=\text{CH}) (\text{CH}_3)_2\text{SiO}_{1/2}$  and  $\text{SiO}_{4/2}$  units, and resins composed of the  $(\text{CH}_2=\text{CH}) (\text{CH}_3)_2\text{SiO}_{1/2}$ ,  $(\text{CH}_2=\text{CH})\text{SiO}_{3/2}$ , and  $\text{SiO}_{4/2}$  units.

5. A composition in accordance with any of Claims 1 to 4 wherein said epoxy-functional organosilicon compound (F) is selected from the group consisting of



6. A composition in accordance with any of the preceding claims further comprising (H) a cure retarder.
7. A method of coating an article of manufacture comprising, applying the composition according to any of the preceding claims to a synthetic fabric and then curing the composition to produce said article.
8. An article in accordance with Claim 7 wherein said synthetic fabric is selected from the group consisting of polyamide fibers, aramid fibers, polyester fibers, polyetherimide fibers, sulfone fibers and carbon fibers.